

Applicant : Vladimir Andreevich Bushuev  
Serial No. : 09/649,431  
Filed : August 25, 2000

d) Remarks:

Reconsideration and allowance of the present application in view of the foregoing amendments and accompanying remarks are respectfully requested.

Claims 8 was pending. By this amendment, claim 8 is being cancelled and new claims 9 and 10 are being added. Support for these new claims is shown in the attachment of Exhibit C.

In the Office Action dated October 20, 2003, the Examiner rejected claim 8 as being allegedly anticipated by U.S. Patent No. 4,265,732.

Without conceding the correctness of this rejection, but solely to advance prosecution, applicant has cancelled claim 8 and has added process claims 9 and 10.

The invention as defined in claim 9 is not disclosed in the prior art cited, including U.S. Patent No. 4,265,732 to Dinulesui.

A difference of pyrolysis process according to the claimed invention and the process according to US Patent 4,265,732 consists in type of pyrolysis reactor used in these processes. Type of reactor defines kinetics of chemical reactions which differs considerably in the new process from kinetics of chemical reactions in the process used by US Patent 4,265,732.

Reactor used in the process on US Patent 4,265,732 is configured as axial type multistage blade machine of conventional structure driven by gas-turbine engine. Each stage of this axial blade

Applicant : Vladimir Andreevich Bushuev  
Serial No. : 09/649,431  
Filed : August 25, 2000

machine is formed by one row of movable blades of rotor and by one row of stationary blades of stator. Gaseous feedstock enters into the first stage of this axial blade machine through inlet nipple and subsequently passes in series through all other stages. The streamlines of fluid form cylindrical surfaces, which are concentric with rotor axis. Temperature of a flow rises during pass through each stage at the expense of heat generated directly inside work medium due to hydrodynamic drag of rotor blades. Then pyrolysis products are quenched and removed through outlet nipple. Thus the temperature of process stream increases by degrees, from an initial value at which a feedstock enters into the reactor from an outside source up to maximum value and then the temperature is reduced. In various points of reaction zone a pressure, temperature and chemical composition of a process stream are different. Duration of process stream heating to maximum pyrolysis temperature presents a considerable part of total time of this mixture residence inside this reactor. Process stream passes through reactor parts positioned in series only once, and recirculation of gaseous process stream is absent. Because of all said above features the reactor of US Patent 4,265,732 relates to flow reactors of "perfect displacement". Kinetics of reactions in this reactor is practically the same that in conventional tubular cracking furnace which relates to a class of flow reactors of "perfect displacement" too.

In the claimed process of the present application a reactor is used having internal recirculation of the process stream. This reactor is configured as a blade machine in which a torque is transmitted from rotated shaft to stationary housing by means of ring vortex of medium filling a work cavity. Hollow housing of the reactor has an inlet nipple and an outlet nipple and stationary blades. Rotatable wheel having work blades is positioned inside this housing. The

Applicant : Vladimir Andreevich Bushuev  
Serial No. : 09/649,431  
Filed : August 25, 2000

housing and the wheel form together an annular work cavity where stationary blades and work blades are arranged. The work cavity is so configured and the stationary and work blades are so positioned in this cavity and are so profiled that a ring vortex flow is created in this cavity when the work wheel is rotated. Mechanical energy is converted into a heat, which is generated directly inside the process stream. Inlet stream continuously enters through inlet nipple into the work cavity and is mixed with hot process stream. By reason of this a heating of inlet stream up to pyrolysis temperature is performed during a negligible time in comparison with residence time. Product stream is continuously removed from the work cavity through outlet nipple. A temperature, pressure and chemical composition of a process stream are practically equal in all points of work cavity. Because of said features, the reactor in the process claimed in the present application is flow reactor of "perfect mixing". Kinetics of chemical reactions in this reactor differs in principle from kinetics of reactions in reactor covered by US Patent 4,265,732.

Difference in kinetics of chemical reactions is a cause that at the same process conditions a product stream contains more low olefins when using the currently claimed process than the process of US Patent 4,265,732. This results from phenomenon that hydrogen, which is one of the final pyrolysis products, is homogeneous catalyst of primary reactions promoting formation of low olefins and at the same time it is homogeneous inhibitor of secondary reactions in the result of which the olefins are wasted.

New pyrolysis process enables use for its realization of a reactor of simpler configuration than reactor in the process according to US Patent 4,265,732. This new reactor may have only one row of work blades and only one row of stationary blades in its work cavity

Applicant : Vladimir Andreevich Bushuev  
Serial No. : 09/649,431  
Filed : August 25, 2000

that enables to fabricate it at modern state of technique of gas-turbines and materials production.

If a telephone interview would be of assistance in advancing prosecution of the subject application, the undersigned attorney invites the Examiner to telephone him at the telephone number provided below.


No fee is deemed necessary in connection with the filing of this Amendment. If any additional fee is necessary, authorization is hereby given to charge the amount of any such fee to Deposit Account No. 03-3125.

Respectfully submitted,

I hereby certify that this correspondence is being deposited this date with the U.S. Postal Service with sufficient postage as first class mail in an envelope addressed to:

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

 4/16/04  
Peter J. Phillips Date  
Reg. No. 29,691

  
Peter J. Phillips  
Registration No. 29,691  
Attorney for Applicant  
Cooper & Dunham LLP  
1185 Avenue of the Americas  
New York, New York 10036  
(212) 278-0400

5

10

C10 G9/16

Process for producing low-molecular olefins by pyrolysis of hydrocarbons (~~and related apparatuses~~)

15

#### **Field of the invention**

The invention relates to the petrochemical industry(~~In one aspect, it relates to the process for~~) **specifically to the** production of low-molecular olefins by thermal cracking (pyrolysis) of hydrocarbons. (~~In another aspect, it relates to the reactor for use in this process. In another aspect, it relates to apparatus for quenching cracked gas for use in this process.~~)

20

#### **Background of the invention**

At present a thermal pyrolysis of hydrocarbons is the basic process of commercial production of low-molecular olefins - ethylene and propylene. As a feedstock there are used hydrocarbons which molecule has two or more atoms of carbon. In industry there are generally used gases of petroleum refining, as well as naphtha and gas oil fractions.

25

In generally accepted technology a feedstock (~~evaporated and~~) mixed with steam **and preheated**, is supplied into a cracking tube located inside radiant section of pyrolysis furnace, wherein the mixture is rapidly heated. Pyrolysis reactions proceed with large absorption of heat. A (~~cracked gas~~) **product stream** having the outlet temperature 750-950°C is quenched and transported into a gas fractionating (~~plant~~) **installation**, in which ethylene, propylene, butadiene, methane, hydrogen and other pyrolysis products are separated. Ethylene is the most valuable product of pyrolysis.

30

(~~During pyrolysis of hydrocarbons a pyrocarbon is always evolved, part of which in the form of soot particles is carried away by flow of cracked gas, but the another part forms coke deposits on the walls both of cracking tubes and downstream apparatuses as well. Coke~~)

~~deposits increase a pressure drop through cracking tubes and deteriorate a proper heat transfer into reaction zone, resulting in overheating the cracking tubes, decrease in productivity of pyrolysis plant and decrease in yields of low-molecular olefins. Therefore coke deposits are periodically removed, usually this is performed by burning out with air or air-steam mixture.)~~

5        Among reactions of thermal pyrolysis there can be distinguished: the primary reactions resulting in formation of olefins and the secondary ones, during which formed olefins are wasted. With temperature increase these reactions are accelerated, both primary and secondary, but the rate of primary reactions increases quicker than the rate of secondary ones. The rate of primary reactions does not depend on pressure, whereas the rate of secondary reactions  
10       decreases with pressure decrease. Therefore, to increase the olefin yields there ~~(strive)~~ **is a need** to decrease hydrocarbon partial pressure in ~~(reaction zone)~~ **the work cavity** and increase the process temperature within said limits. The hydrocarbon partial pressure can be decreased by adding a steam-diluent. An optimal amount of steam-diluent depends on **the** composition of **the** hydrocarbon feed. For light feedstock - ethane or propane - the amount of steam usually is  
15       20-40% of feedstock mass. For heavy feedstock, **such** as gas oils, ~~(an)~~ **the** amount of **a** steam ~~(usually is)~~ **can be** 80-100% of feedstock mass. It is undesirable to increase the pyrolysis temperature above 950-1000°C, because this accelerates sharply coke formation and causes ~~(growth)~~ **increase in yield** of less valuable acetylene yield at the expense of ethylene.

**Essential component of pyrolysis plants is the means for quenching of product stream leaving reactor to the temperature of stopping undesirable secondary reactions. The quenching can be both direct - by injection of steam, water or light pyrolysis tar - and indirect - by using a heat exchanger. The direct quenching is usually applied in thermal cracking of gas oils. In thermal cracking of light hydrocarbons the indirect quenching in heat exchanger apparatus is usually applied generating simultaneously a high pressure steam.**

**During pyrolysis of hydrocarbons a pyrocarbon is always evolved, part of which in the form of soot particles is carried away by the product stream, but the another part forms coke deposits on the walls both of cracking tubes and downstream apparatuses as well. Coke deposits increase a pressure drop through cracking tubes and deteriorate a proper heat transfer into reaction zone, resulting in overheating the cracking tubes, decrease in productivity of pyrolysis plant and decrease in yields of low-molecular olefins. Therefore coke deposits are periodically removed, usually this is performed by burning out with air or air-steam mixture.**

(Among) **Following** disadvantages of ~~(commercial tubular cracking reactor the~~

following) hydrocarbon pyrolysis in tubular furnaces is noteworthy:

a. it is necessary to transfer a large amount of heat into the reaction zone through the cracking tube walls. Because of large heat flows the temperature of the cracking tube wall much exceeds the temperature of a process stream causing an intensive coke formation and decrease in desired products yield. It is impossible to decrease the pressure in the zone of pyrolysis because of the necessity to provide a high rate of feedstock flow through this zone required by conditions of heat transfer;

b. (a) the rate of feedstock heating through the cracking tube is insufficient. (~~Because of this a starting~~) So an initial amount of desired olefins formed at relatively low temperatures and carried further by feedstock flow through more and more intensively heated zones resides an excess time under conditions, when secondary reactions proceed with grate intensity. This disadvantage becomes (~~apparent~~) greatly evident in pyrolysis of wide petroleum fractions, such as naphtha or gas oil, which contain (as) both easy cracked high-molecular hydrocarbons (~~cracked easily, as~~) and low-molecular hydrocarbons cracked (~~at~~) under higher temperatures.

To eliminate said disadvantages, the processes for producing olefins by the thermal decomposition of hydrocarbons were offered, in which heat is not transferred into the reaction zone through boundary of this zone.

US Patent 5300216 discloses method and apparatus for thermal cracking hydrocarbons in the presence of steam by passing through stationary shock wave of high intensity. A steam superheated in a tubular heater to (~~the~~) a temperature of about 1000°C is introduced at (~~the~~) a pressure of about 2.7 MPa through a supersonic nozzle into a reactor comprising series-positioned mixing and pyrolysis zones. In the mixing zone the hydrocarbon feed - ethane - preheated to the temperature of about 627°C is introduced through mixers into supersonic flow of steam. The (~~R~~)resulting mixture forms a supersonic process stream, which has a temperature lower than that required to initiate pyrolysis reactions. Between the said mixing and pyrolysis zones a straight compression shock - continuous-standing shock wave - is created. In this compression shock a kinetic energy of the supersonic process stream is converted into the heat. Immediately downstream of the compression shock the velocity of the process stream falls to subsonic level, and the temperature rises up to about 1000°C at (~~the~~) a pressure of about 0.9 MPa abs. The process stream passes the pyrolysis zone for 0.005-0.05 sec. while its temperature decreases to about (~~to~~) 863°C at the expense of heat absorbed by pyrolysis reactions. Conversion of ethane into ethylene achieves 70%. (~~Cracked gas~~) The product stream passes quenching apparatus and downstream heat exchangers, and further is transported to gas fractionation (~~separation~~). In this apparatus all said above disadvantages of

tubular pyrolysis reactors are eliminated. The feedstock reaches maximum pyrolysis temperature (~~at most~~) especially rapidly, and the boundary (walls) of the pyrolysis section are not used for transfer of heat into reaction zone. But at the same time the required amount of steam per hydrocarbon mass must be about 500-667%. (~~By reason~~) Because of this the energy expenses per unit of produced ethylene are excessively high and (~~unable to~~) can not be essentially decreased. (~~This renders the~~) Thus this apparatus noncompetitive at current interrelation of energy costs with olefin costs.

US Patent 5597537 discloses a process for fluidized catalytic cracking of hydrocarbon feed stream. This process comprises contacting the hydrocarbon feed stream with a dust catalyst at an initial temperature 664°C in a riser. Heat required for the cracking is transferred to process stream from particles of catalyst, and temperature of the catalyst decreases to 532°C. Then hydrocarbon products are separated from a coked catalyst, and coked catalyst passes to a regenerator. Here the coke from said catalyst is combusted by hot air to produce regenerated catalyst, and catalyst temperature increases. Regenerated catalyst passes into riser again. In this apparatus a heat is not transferred into reaction zone through boundary of this zone.

Unfortunately, high severity of destruction process, typical for pyrolysis of hydrocarbons in tubular furnaces, in this apparatus is impossible. This is a cause on which the best yield of ethylene in this apparatus does not exceed 5...7%, and so this apparatus is not used for commercial producing of ethylene.

~~(US Patent 4426278 discloses tubular pyrolysis reactor including a steam superheater, an apparatus for mixing superheated steam with hydrocarbon and a cracking tube positioned inside radiation block. Coming from the superheater a steam with the temperature 1000-1500°C is mixed with hydrocarbon feed, so as to obtain immediately a temperature of resulting mixture required to initiate pyrolysis reactions. In this reactor the said above disadvantage (b) is partly eliminated. However, at the temperature 1100°C the steam must be supplied in amount 185-275% in a ratio to hydrocarbon mass, and at the temperature 1430°C about 120%. Preparation of superheated steam with such high temperature is extremely difficult and energy expenses are excessively high.~~

~~US Patent 3579601 discloses tubular pyrolysis reactor in which a feedstock is introduced into cracking tube at several points spaced out along its length. Every portion of introduced feedstock reaches at once a temperature enough for starting pyrolysis reactions due to practically instant mixing with hot pyrolyzed gas incoming from upstream cracking tube run. Pyrolysis is maintained further by heat supplied through cracking tube walls. This invention~~



eliminates partly the disadvantage (b), but the disadvantage (a) remains. The yields of olefins and other unsaturated hydrocarbons are increased, and coke deposition and methane formation are decreased. The disadvantage of this invention is an intricate configuration of the cracking tubes making difficulties for positioning it within radiant chamber of a heater.

5       USSR Author's Certificate 1189871 discloses process for thermal cracking naphtha and gas oils. A feedstock is separated into several fractions boiling out in intervals every 20-40°C. Such prepared narrow fractions are pyrolyzed in individual cracking tubes under optimal thermal conditions suitable for each fraction. This process enables to diminish the disadvantage (b), increase a yield of low molecular olefins and decrease a coke formation, but technical  
10       realization of this process is associated with intricacy of radiant chamber structure because it necessitates to create individual thermal conditions for several cracking tubes under unsteady interrelation of feedstock flow rates in them.

US Patent 4265732 discloses process for thermal cracking gaseous hydrocarbon feed in a reactor constructed as multistage blading machine of axial type. A heat required for pyrolysis is  
15       generated directly inside a volume of reacting gas due to hydrodynamic drag of the rotor blades rotated therein by a drive. This invention eliminates completely the disadvantage (a), but the disadvantage (b) is not eliminated. Needed for process realization an axial type multistage blading apparatus capable of operation under the temperatures of hydrocarbon pyrolysis has not been fabricated. )

20       US Patent 4265732 discloses a process for thermal cracking gaseous hydrocarbon feed, wherein the heat required for pyrolysis is generated directly in a process stream due to hydrodynamic drag of the rotated blades. Pyrolysis takes place in a reactor designed as a multistage blade machine of axial type containing alternating rotating blade rows and stationary blade rows positioned in series. Desired profiles of a pressure and temperature  
25       along the reactor length are reached by properly profiling of these blades. The reactor boundary is not used for transfer of heat into the reaction zone.

This invention eliminates completely the disadvantage (a), but the disadvantage (b) is not eliminated. An axial type multistage blade apparatus is needed to realize this process. This apparatus have to be capable of work at very high temperatures (up to  
30       1050°C) and comprise a great number of stages (up to 43). Difficulties appearing in development of this apparatus are so heavy that such apparatus has not been fabricated.

(US Patent 5271827 discloses tubular pyrolysis furnace provided with adiabatic tube reactor located between cracking tube outlet and an inlet of quenching apparatus. In the adiabatic tube reactor the pyrolysis is carried out at the expenses of intrinsic heat of reacting

fluid without heat supply from outside. A use of the adiabatic tube reactor enables to economize on energy expenses required for pyrolysis.

Essential component of pyrolysis plants is the means for quenching cracked gas leaving reactor to the temperature of stopping undesirable secondary reactions. The quenching can be both direct — by injection of steam, water or light pyrolysis tar — and indirect — by using a heat exchanger. The direct quenching is usually applied in thermal cracking of gas oils. In thermal cracking of light hydrocarbons the indirect quenching in heat exchanger apparatus is usually applied generating simultaneously a high pressure steam.

PCT Application WO 95/32263 claims apparatus for quenching cracked gas. This apparatus comprises two spaces separated by a wall. A cracked gas flows in tubes, which form one of the said spaces, and a cooling water is boiled in the another space. Because of small diameter of these tubes the apparatus of such type causes great flow resistance and is disposed also to coking. Usually the pressure drop through purged apparatus is not less 0.02–0.03 MPa, and in coked state it reaches 0.07 MPa and higher, that increases the pressure in upstream pyrolysis reactor and thereby decreases olefins yield. It could be possibly to decrease the pressure drop through apparatus by increase a diameter of heat transfer tubes, but such solution is impermissible since it results in decrease of quenching rate.)

**Thus all known methods of low-molecular olefins production by thermal pyrolysis of hydrocarbons when a heat is not transferred into zone of reaction through boundary of this zone are not suitable for commercial using.**

**Thereby, attempts to develop a method of pyrolysis of hydrocarbons free of disadvantages (a) and (b) were not successful and at present the thermal pyrolysis of hydrocarbons in tubular furnaces is a single commercial method of the ethylene production.**

**In prior art there are known and widely used hydrodynamic devices, in which a torque is transferred from rotating shaft to stationary housing by ring vortex of medium filling work cavity. In these devices mechanical energy is converted into heat that is generated directly inside work medium and heats it. Such hydrodynamic devices having small overall dimension can transfer a maximum torque and absorb maximum power.**

**Here and hereinafter wording "ring vortex" means a vortex with the ring core, thereby, word "ring" pertains to the form of vortex core. Streamlines of such vortex are of the form of spirals convolute in ring.**

**US Patent 2672954 discloses hydrodynamic dynamometer. Housing and rotatable rotor located inside it form together two annular work cavities filled with liquid. In the**

work cavity the blades fixed on the rotor and directing blades fixed on the housing are located. Said cavities are formed and the said blades are configured and positioned so that in each cavity a ring vortex is created when the rotor is rotated. This ring vortex transfers a torque from rotor to housing of device. Cold work liquid is supplied into this device and hot one is withdrawn from the device through respective nipples communicated with work cavity.

US Patent 3537264 discloses hydrodynamic brake. Housing and rotatable rotor, which is located inside it, form together an annular work cavity filling with work fluid. This work cavity through respective channels is communicated with inlet and outlet nipples for transporting the work fluid. In the work cavity the rotor blades and stationary directing blades are located. The said cavity is formed and the said blades are configured and positioned so that a ring vortex is created when the rotor is rotated. This ring vortex transfers a torque from rotor to housing of device. The work fluid in this device is a liquid or gas (air, for example).

US Patents 4864872, 5147181, 5571975 disclose fluid torque transfer devices, which constructions are similar to the hydrodynamic brake covered by US Patent 3537264. The said devices and hydrodynamic brake on US Patent 3537264 differ in form and location of work and stationary blades.

#### Summary of the invention

The (purpose) aim of the invention is creation of a process for producing low-molecular olefins by thermal pyrolysis of hydrocarbons(~~reactor for use in this process and quenching apparatus for use in this process~~).

In this process:

(a.) I a heat is not transferred into the reaction zone through (walls closing) boundary of this zone.

(b.) II a heating of hydrocarbon feed to pyrolysis temperature is performed for negligible time in comparison with the residence time (~~duration of pyrolysis reactions~~).

(c.) III (~~an~~) the amount of added steam-diluent per mass of hydrocarbon feedstock does not exceed the limits accepted in existing pyrolysis installations (~~plants~~).

(~~This purpose is reached in the process for producing low molecular olefins by thermal pyrolysis of hydrocarbons comprising preheating and evaporating a starting feedstock; mixing the same with a steam diluent; heating resulting mixture to pyrolysis temperature in a blading rotary reactor; quenching a cracked gas and subsequent separation of it, in this process the reacting mixture is heated to pyrolysis temperature due mixing with hot pyrolyzed gas being~~

circulated in a working cavity of the blading reactor.

Preferably preheating the feedstock and steam diluent is performed in two stages, where the second stage is carried out in a heat exchanger by heat taken away from the cracked gas leaving the reactor.

5 In comparison with the process under US Patent 4265732 the present novel process increases desired olefins yield due to instant heating the reacting mixture up to maximum pyrolysis temperature by mixing with hot gases just pyrolyzed and yet circulated in working cavity of the reactor. The heat of cracked gas leaving the blading reactor is utilized for preheating the feedstock and steam diluent entering into reactor, that enables to simplify a  
10 structure of heat exchanger due to decrease in difference of pressure in heated and cooled sections and reduce also energy expenses for carrying out the process.

Purpose of the invention is reached also by using in the process for producing low-molecular olefins by thermal pyrolysis of hydrocarbons the reactor comprising a housing with directing stationary blades, an inlet nipple for supplying feedstock, an outlet nipple for carrying  
15 off cracked gas and a working wheel provided with a blade crown. The housing has an annular cavity for circulation of hot pyrolyzed gas, where the directing stationary blades are located. This cavity surrounds the blade crown of the working wheel on periphery, and the inlet and outlet nipples are communicated with the said cavity.

As distinct from the reactor under US Patent 4265732 the new reactor enables to heat the  
20 mixture of feedstock and steam diluent to maximum pyrolysis temperature practically instant due mixing with hot pyrolyzed gases, thus resulting higher yields of low-molecular olefins. The another advantage of this reactor is louver damper configuration enabling to make it in one-stage variant and of materials wide known and used presently in technique.

Purpose of the invention is reached also by using in the process for producing low-  
25 molecular olefins by thermal pyrolysis of hydrocarbons the apparatus for quenching cracked gas comprising a heat exchanger having two spaces separated by a wall. This apparatus is provided with a tee and with an ejector comprising a nozzle, admission and mixing chambers. The mixing chamber and one of the tee nipples are communicated with the space of cooled fluid, and the admission chamber is connected with the another nipple of the tee.

30 Such configuration of the apparatus for quenching cracked gas provides both a short time of quenching and small pressure drop through the apparatus as well, so that to obtain decrease in pressure in upstream reaction zone contributing to achievement of increase in low-molecular olefins yield.)

This aim is achieved in the process for producing low-molecular olefins by thermal pyrolysis of hydrocarbons comprising steps:

a) preparation of evaporated feedstock steam mixture,

b) preheating the resulting mixture

5 c) heating said mixture up to pyrolysis temperature,

d) a supply with a heat, which is necessary for pyrolysis, into the process stream,

e) quenching a product stream, and

f) fractionation of the product stream,

in this process

10 in the step a) amount of added steam-diluent per mass of hydrocarbon feedstock does not exceed the limits accepted in existing pyrolysis plants,

steps c) and d) are performed in a reactor, comprising: a hollow housing having a nipple for inlet stream, and a nipple for outlet stream, and stationary blades;

15 a rotatable wheel with a work blades is positioned in said housing so that said wheel with said housing together form an annular work cavity,

said cavity is formed so and said stationary blades and work blades are positioned in said cavity and are shaped to create a ring vortex flow in said cavity when said wheel is rotated, and

20 said nipple for inlet stream and said nipple for outlet stream are communicated with said work cavity,

step c) is performed by mixing of said mixture with hot process stream being circulated in said work cavity, for a negligible time in comparison with the residence time,

25 step d) is performed by using heat, generated directly in the process stream in result of hydrodynamic drag of said rotated work blades.

Reactor used in a process on the invention has annular work cavity in which stationary blades and blades of work wheel are located. When the work wheel is rotated a process stream circulates within this work cavity to create a ring vortex so that each particle of feedstock repeatedly passes through work blade row and stationary blade row.

30 The heat needed for pyrolysis is generated directly inside the process stream as a result of a hydrodynamic drag of the rotated work blades. The work cavity boundary is not used for heat transfer into this cavity and a temperature of this boundary is close to temperature of the process stream.

A ring vortex flow in the work cavity provides transfer of maximum power to the

process stream recirculated within this cavity, which can be achieved at given sizes and speed of rotation of work wheel. The ring vortex flow is used to achieve a high heat-generation per unit volume in the work cavity of a single-stage reactor, i.e. of the reactor having one work blade row and one stationary blade row in the work cavity. The single-stage design of the reactor gives a possibility of its fabrication by using existing materials and conventional gas-turbine technologies. A preheated inlet stream reaches pyrolysis temperature almost instantly due to mixing with hot process stream. By this way the aims (I) and (II) of the invention are achieved.

In the process on the invention, equally as in pyrolysis process in tubular furnaces, a steam-diluent is used for reduction of partial pressure of hydrocarbons in reaction zone, and pressure in work cavity of the reactor is lower than in a cracking tube of pyrolysis furnace. Consequently a steam-diluent content in the inlet stream needed for reduction of the hydrocarbons partial pressure down to the desired value will not be greater than in existing pyrolysis installations. By this way the aim (III) of the invention is achieved.

In the process on the invention, a heating of inlet stream up to pyrolysis temperature is performed by mixing it with hot process stream, which circulate in a reaction zone. That means, that reactor on the invention is reactor with the internal recirculation of process stream, which work process is close to work process of flow reactors of perfect mixing. Because of it the process fundamentally differs from all known processes of hydrocarbon pyrolysis, including the process on the US Patent 4265732 and processes realized in tubular pyrolysis furnaces. In comparison with the process on US Patent 4265732, the present process enables to increase in the low-molecular olefin yield. Opportunity to use a reactor of simpler design is the another advantage.

In accordance with a preferable version of the process on the invention a gas-turbine engine is used as a drive of said reactor, and step (b) is performed in two stages. The first stage of said preheating is carried out in first heat exchanger utilizing heat of exhaust gases of said gas-turbine engine. The second stage of said preheating is carried out in second heat exchanger utilizing heat of hot product stream outgoing from said reactor.

Using of gas-turbine engine as a drive of reactor is preferable because a heat of the exhaust gas can be effectively utilized for evaporation of inlet stream components in the first stage of preheating. But maximum temperature, which can be achieved at this stage, is limited by temperature of exhaust gas of a gas-turbine engine. By this reason a

preheating of the inlet stream up to higher temperature is performed at second stage by utilizing a heat of hot product stream outgoing from the reactor, simultaneously the quenching of product stream is performed. The inlet stream preheating reduces energy consumption for process conducting.

## 5 Brief description of the drawings

Fig. 1 is a schematic view of the installation for realization of the process for producing low-molecular olefins.

Fig. 2 is a sectional view of the reactor for use in the process for producing low-molecular olefins (~~by pyrolysis of hydrocarbons~~).

10 Fig. 3 is a cross-sectional view taken on line A-A in Fig. 2.

Fig. 4 is a sectional view of the radial work(~~ing~~) blade of the reactor.

Fig. 5 is a view on the arrow B in Fig. 4.

Fig. 6 is a sectional view of the apparatus for quenching of product stream (~~cracked gas~~) in the process for producing low-molecular olefins (~~by pyrolysis of hydrocarbons~~).

## 15 Description of the preferred embodiments

The installation (Fig. 1) for realization of the process includes preheater 1, apparatuses 2 and 3 for quenching of product stream (~~cracked gas~~), reactor 4, gas-turbine engine 5 connected with reactor 4 by shaft 6, and with the preheater 1 by exhaust pipe 7.

Preheating a feedstock and steam-diluent in the first stage is carried out in the preheater

20 1. The hydrocarbon feed from outside source (not shown in drawings) is conveyed by pressure into the preheater 1 configured as a shell-tube heat exchanger. The exhaust gas from the gas-turbine engine 5 is discharged into the intertubular space of this heat exchanger. From an outside source (not shown in drawings) water is conveyed by pressure into the preheater 1 where the water it is evaporated, and resulting steam-diluent is mixed with the hydrocarbon

25 feed.

Preheating a feedstock and steam-diluent in the second stage is carried out in the apparatuses 2 and 3 for quenching of product stream (~~cracked gas~~) by utilization of heat of product stream (~~cracked gas~~) leaving the reactor. Detailed description of the apparatus for quenching of product stream (~~cracked gas~~) will be given below.

30 The mixture of feedstock and steam-diluent from the apparatuses 2 and 3 (~~for quenching cracked gas~~) is conveyed into the (~~blading~~) reactor 4. Hot (~~pyrolyzed gases~~) process stream are circulated within the work(~~ing~~) annular cavity of the reactor, and the heat needed for pyrolysis is generated directly inside the volume of process stream (~~reacting mixture~~) due to hydrodynamic drag effect of rotating work(~~ing~~) wheel provided with the blades. Initial heating

of the particles of feedstock up to pyrolysis temperature is performed by mixing them with the hot (~~pyrolyzed gases~~) process stream for the negligible time in comparison with residence time (~~duration of pyrolysis reactions~~). Detailed description of the reactor structure will be given below.

5 The product stream (~~cracked gas~~) from the reactor 4 is conveyed into the quenching apparatuses 2 and 3 through interconnecting pipes having smooth shape to prevent formation of flow detachment zones. All these interconnecting pipes are equalized in volume.

The product stream (~~cracked gas~~) is quenched in the apparatuses 2 and 3 and then transported into a gas fractionating installation (~~plant~~) (not shown in the drawings). In the Fig. 10 1 there are depicted two apparatuses for quenching of product stream (~~cracked gas~~), but the number of this apparatus is not limited in the (~~invention~~) practical realization of the invention.

As a reactor drive the gas-turbine engine 5 is applied. Shown in Fig. 1 the gas-turbine engine (~~is of~~) works on a simple thermodynamic cycle (~~without~~) has no intermediate heaters and coolers of the work(~~ing~~) fluid. As a drive there can be also used gas-turbine engines 15 operating (~~in~~) on more (~~compound~~) complex cycle, as well as steam turbine or electric motor.

The amount of steam being mixed with the hydrocarbon feed and tolerance final temperature depend on the composition of the feedstock. If a feedstock is (~~the~~) an ordinary gaseous hydrocarbons, the amount of added steam (~~may~~) should be to 30-40% in (~~ratio~~) proportion to hydrocarbon mass, and the temperature of the inlet stream (~~reacting mixture~~) 20 after second preheating should not exceed 650°C. If the ordinary liquid hydrocarbons - such as naphtha or gas oils - are used as a feedstock, the steam may be added in an amount (~~to~~) of 80-100% in (~~ratio~~) proportion to hydrocarbon mass, and relevant temperature of the inlet stream (~~reacting mixture~~) after the second preheating should not exceed 550-600°C.

The basic parameters defining operation of the reactor are interrelated (~~tied together~~) by 25 the following relationship:

$$\tau = V \times d \times H / P$$

where:

$\tau$  (sec) is the mean residence time of the process stream (~~reacting mixture~~) in the reactor;

30  $V$  (m<sup>3</sup>) is the volume of the reactor work(~~ing~~) cavity (~~space~~);

$d$  (kg/m<sup>3</sup>) is the mean density of the process stream (~~reacting mixture~~) within the reactor work(~~ing~~) cavity (~~space~~);

$H$  (J/kg) is the energy transferred into the process stream (~~reacting mixture~~) within the reactor work(~~ing~~) cavity (~~space~~);



P (W) is the power transferred into the reactor work(~~ing~~) cavity (~~space~~).

The energy, which should be transferred into the process stream (~~reacting mixture~~) within the reactor work(~~ing~~) cavity (~~space~~), is close (~~near~~) to the amount of heat transferred into process stream flowing through a radiant coil in conventional tubular pyrolysis furnaces operating with the same kind of feedstock. In pyrolysis of ethane this energy should be about 2.5-3.4 MJ per kg of feed/steam mixture. In pyrolysis of other kinds of hydrocarbon this energy should be about 1.7-2.3 MJ/kg.

The mean residence time of (~~reacting mixture~~) the process stream inside the reactor work(~~ing space~~) cavity can be about 0.03-0.1 sec.

10 The period of time for heating the incoming feed/steam mixture from the temperature when entering into the reactor up to pyrolysis temperature is defined by the duration of mixing with the process stream (~~reacting mixture~~) being processed and does not exceed 0.001 sec. It is negligible short time in comparison with the residence time of the process stream (~~reacting mixture~~) within a work(~~ing~~) cavity (~~space~~) of the reactor.

15 The mean density of the process stream (~~reacting mixture~~) is defined by average pressure, by average temperature in work(~~ing~~) cavity (~~space~~) of the reactor and by average molecular mass of the process stream (~~reacting mixture~~).

The average pressure within work(~~ing~~) cavity (~~space~~) of the reactor can be set in the range (~~arranged of~~) 0.05-0.2 MPa (abs), preferably 0.08-0.12 MPa (abs).

20 The average (gas) the process stream temperature in the reactor work(~~ing~~) cavity depends on the feedstock composition, assigned conversion and residence time within work cavity (~~reaction zone~~). Light feedstock and high conversion require the higher temperatures, but heavy feedstock - as atmospheric and vacuum gas oils - and low conversion require lower temperatures.

25 The (~~Θ~~)operator sets the (gas) temperature of the process stream in the work(~~ing~~) cavity of the reactor and the rates of hydrocarbon feed and water for preparing steam-diluent. The set temperature is maintained by automatic control system regulating a rate of fuel gas feeding the gas-turbine engine. (~~So~~) Thence the temperature in the work cavity (~~reaction zone~~) of the reactor is regulated as in principle as it is done in the conventional tubular furnace - by changing a rate of fuel gas in ratio to a rate of feedstock. A difference is that transient processes in the novel reactor are ended faster in 10-100 times.

30 To remove a coke from the reactor and the apparatuses for quenching (~~cracked gas~~) of the product stream it is necessary to stop supply of hydrocarbon feed into the preheater 1. The temperature in the work(~~ing~~) cavity of the reactor must be maintained much the same as

the temperature during pyrolysis. In the result of gasification reactions a superheated steam removes the coke deposits from the reactor 4 as well as from transfer tubes and apparatuses 2 and 3 for quenching of product stream (~~cracked-gas~~). Outgoing flow is conveyed into afterburning installation (not shown in drawings). The process of decoking is (~~controlled~~ through) checked by analysis of (~~outgoing-flow~~) the output stream. When the contents of hydrogen, carbon oxide and carbon dioxide (~~fall~~) decreased down to beforehand assigned values, decoking is stopped and supply of hydrocarbon feed (~~is-renewed~~) must be resumed. The advantage of such burning-out in comparison with air or air-steam burning-outs (~~are~~) is endothermicity of the proceeding reactions eliminating a danger of local overheating construction materials. The another advantage is that reducing medium inside the reactor remains at all regimes of operation, enabling fabrication of the most important reactor elements of the heat-resistant alloys on base of heat-proof metals unstable under oxidizing conditions, for example of the alloys on base of tungsten or molybdenum, or niobium.

In the present process the pyrolysis of feedstock proceeds in series in the work(~~ing~~) cavity, and further in transfer pipelines conveying (~~pyrolyzed-gas~~) the product stream to the quenching apparatuses. The hydrodynamic regime that is realized within the reactor work(~~ing~~) cavity is close to regime peculiar to apparatus of (~~ideal~~) perfect mixing, where concentrations of reactants are homogeneous within this cavity. The process essentially differs by this from process realized in conventional tubular reactors and from the process disclosed by US Patent 4265732 as well.

Since the pyrolysis in the reactor work(~~ing~~) cavity (~~space~~) proceeds in presence of just cracked products of high concentration, the pyrolysis reactions are accelerated due to autocatalysis phenomenon. Because of (~~it~~) this the pyrolysis can be carried out also at lower temperature thus increasing the process selectivity. This is confirmed by experimental data on pyrolysis of hydrocarbons in presence of hot pyrolyzed gases, indicated in US Patent 3579601.

Inside transfer pipelines the pyrolysis proceeds adiabatically, without supply of heat from outside. The hydrodynamic regime realized here is close to regime peculiar to apparatus of (~~ideal~~) perfect displacement as in tubular reactors. This adiabatic run enables to (~~economize on~~) reduce energy expense for carrying out the pyrolysis process and (~~enables-also~~) to increase the olefin yields.

The (~~rotary-blading~~) reactor (Fig. 2 and 3) for hydrocarbon pyrolysis comprises a housing including casing 8 with lids 9 and 10. Inner surfaces of the casing 8 and the lids 9, 10 are covered with heat insulators 11, 12 and 13. The housing comprises also a heat resistance skin formed by element 14 fastened together with the casing 8, and elements 15 and 16 fastened

together with the lids 9 and 10. ~~(With)~~ **By means of** the element 14 the directing blades 17 and 18 are fastened together. Directing blades 19 and 20 are fastened together with the elements 15 and 16. The casing 8 is provided with nipples 21 for ~~(supplying feedstock)~~ **inlet stream** and nipples 22 for carrying off the **product stream** ~~(cracked gas)~~. A rotor consists of shaft 23 and  
 5 work(~~ing~~) wheel 24 provided with work(~~ing~~) blades 25. The latter form the ~~(blade crown)~~ **blading** of the work(~~ing~~) wheel 24. The shaft 23 is supported by radial 26 and radial-thrust 27 bearings and is sealed up by double labyrinth packings 28 and 29 into channels of which a steam is injected from outside (not shown in the drawings).

Each work(~~ing~~) blade 25 (Fig. 4 and 5) has a tail 30, by which they are fixed on a rim of  
 10 the work(~~ing~~) wheel 24 forming a dovetail lock. In the blade 25 the radial channels 31 are made for passing ~~(a mixture of feedstock with steam diluent)~~ **an inlet stream** used as a cooling agent.

The reactor operates in the following way. Through the ~~(supplying)~~ **inlet** nipples 21 ~~(a mixture of evaporated feedstock with steam diluent)~~ **an inlet stream** enters into a gap  
 15 between the casing 8 and the heat resistant skin, passes further through the channels made in the work(~~ing~~) wheel 24 and in the work(~~ing~~) blades 25 and enters into the annular work(~~ing~~) cavity where the work(~~ing~~) blades 25 and the directing blades 17, 18, 19, 20 are arranged. **The** ~~(P)process(ed) (fluid)~~ **stream** being circulated within the annular cavity comes into multiple contacts in turn with the stationary directing blades and rotating work(~~ing~~) blades, thereby  
 20 creating streamlines in the form of two spirals rolled up into vortex rings of right and left directions. Thus two communicating circuits of ~~(pyrolyzed gas)~~ **process stream** circulation are created. ~~(A-h)~~Heat being absorbed by endothermic reactions, which continuously proceed within the reactor work(~~ing~~) ~~(space)~~ **cavity**, is compensated by influx of heat ~~(arose)~~ **arisen** from converting kinetic energy into heat.

A power transferred into the said circuits is proportional to the rotor peripheral velocity and meridional velocity and density of the processed fluid. With increase of meridional velocity the power, dissipated by rotor, increases until this velocity reaches 0.64-0.7 sonic velocity in this fluid, (e.g.) **i.e.** about 400-500 m/s. At higher meridional velocities the power dissipated by rotor into ~~(reaction zone)~~ **the work cavity** sharply decreases because of decrease  
 30 of the fluid density averaged along a height of the blade. This is connected with a fact, that in the core of **ring** vortex ~~(ring)~~ the pressure is lower than on its periphery, and this pressure decrease depends on meridional velocity of the fluid.

During every passing through blad(~~e crown~~)**ing** of a work(~~ing~~) wheel the reacting fluid acquires an additional kinetic energy, which for the time before next passing is converted into a

heat. This occurs partly due to passing the fluid through stationary compression shocks arising in places of local transition of the fluid through sonic barrier, and partly due to vortex formation. The additional kinetic energy is proportional to the rotor peripheral velocity and meridional velocity of the fluid. For example, at the rotor peripheral velocity 300-400 m/s this energy can be about 70-150 kJ/kg. During the time of residence within the circuit every particle of feedstock should pass over the rotor work(ing) blades several tens times on average.

The advantage of the rotary blad(ing)e reactor in comparison with conventional tubular reactors is that (~~its walls bounding the reaction zone~~) the boundary of the work cavity are not used for heat transfer, therefore, (~~in absence of~~) if a cooling is absent (~~of the walls~~), (~~their~~) the boundary temperature differs from the temperature of (~~reacting fluid~~) the process stream insignificantly. Lower (~~wall~~) boundary temperature and lower pressure in the (~~reaction zone~~) work cavity in comparison with the same in conventional tubular reactors (~~enable~~) are reasons to expect increas(e)ing in the process selectivity and (~~increase~~) growth in desired product yields when processing the same kinds of feedstock. Short time of the installation starting and possibility of full automation of its operation and control contributes to increase in the desired product yields.

The apparatus for quenching of product stream (~~cracked gas~~) (Fig. 6) includes a "tube-in-tube" heat exchanger comprising outer tube 32 and inner tube 33, inlet 34 and outlet 35 nipples for product stream (~~conveying cracked gas~~), inlet 36 and outlet 37 nipples for conveying cooling agent communicated with intertubular space, and ejector comprising nozzle 38, an admission chamber 39 and a mixing chamber 40. The nozzle 38 is connected with the inlet nipple 34. The inner tube 33 is connected by one end with the mixing chamber 40 and by another end through the tee 41 with the admission chamber 39 and the product stream (~~cracked gas~~) outlet nipple 35. Outer surfaces of the quenching apparatus are covered by heat insulator 42.

Hot product stream (gas) entering through the nipple 34 (~~is formed by the~~) passes into nozzle 38. Nozzle 38 forms (~~into~~) a jet which sucks cooled gas (~~being in~~) from the admission chamber 39. The (~~R~~)resulting mixture flowing through the inner tube 33 (~~cools down~~) is cooled thus, giving back its heat to the fluid flowing through the intertubular space between the outer tube 32 and the inner tube 33 in direction from the nipple 36 to the nipple 37. (~~Some~~) A part of the cooled mixture enters into the admission chamber 39, and residual part is removed out of the apparatus through the nipple 35.

Outgoing from the nipple 35 cooled product stream (~~cracked gas~~) can have the temperature (~~about~~) from 350 to 400°C. Mass rate of the mixture in the inner tube exceeds

about in 2-2.5 times the rate of the product stream (~~cracked gas~~) coming from the reactor, and the mixture being formed in the mixing chamber 40 can have the temperature about 620-660°C.

Duration of (~~cracked gas~~) the product stream quenching is defined only by the time of  
 5 mixing the jet formed by the nozzle 38 with cooled gas from the mixing chamber 40 and can be of some milliseconds. Diameter of the inner tube 33 must be enough that it should not cause considerable pressure resistance.

A heat exchanger included in the apparatus for quenching of product stream (~~cracked gas~~) can be of any (~~different~~) other structure than "tube-in-tube" type. Small difference in  
 10 pressure between heated and cooled fluids and low values of pressure enable to apply a plate heat exchanger or any others having (~~less~~) lower both a mass and a cost in comparison with quenching apparatus (~~used~~) usually used.

#### Commercial applicability

(~~The invention is intended for use in ethylene production plants as modernized as newly~~  
 15 ~~constructed, instead of tubular pyrolysis furnaces. Composition of pyrolysis products prepared on the novel process differs insignificantly from one in existing furnace installations operating with the same feedstock. Therefore a use of the process should not practically demand to change fractionating and gas separation plants.~~

~~For novel installations there can be used gas turbine engines of small size without~~  
 20 ~~intermediate preheaters and coolers of a working fluid. Best samples of such engines can have efficiency 42% at the temperature of exhaust gas 570°C. High temperature of exhaust gas enables to use effectively its heat for evaporating and preheating feedstock, for steam diluent preparation and also for superheated steam generation in amount enough to drive compressors of a gas separation plant. As a fuel there can be used natural gas or methane-hydrogen fraction~~  
 25 ~~separated from cracked gas in gas separation plant. A noise made by gas turbine engine does not exceed the noise made by acoustic gas burners in conventional pyrolysis furnaces. To carry off an exhaust gas from gas turbine engines there can be used chimneys similar to ones usually used in tubular furnaces. For pyrolysis plant with capacity on hydrocarbon feed about 80,000 tons per year it should be required a gas turbine engine of power about 8-12 megawatts. Such~~  
 30 ~~engines are fabricated serially and are capable of long-time operation under conditions of continuous loading, as gas blowers in gas pumping stations of arterial gas pipelines. Full durability of such engines can run up to 100,000 hours.~~

~~In designing novel pyrolysis installations it might be as practicable to use materials, operational experience and technologies used by producers of gas turbine engines. If a reactor~~

and its gas turbine drive will be made in the same factory, the pyrolysis installation can be configured on a common framework in the form of compact aggregate of full readiness.)

Novel process for producing low-molecular olefins is intended for use instead conventional process of pyrolysis of hydrocarbons carried out in tubular furnaces. The present invention can be applied as in building of new ethylene plants and in modernization of existing ethylene plants as well.

Calculations show that in installation based on rotary blade reactor driven by gas-turbine engine of 10...16 MW power a capacity on processed feedstock (naphtha) will be 14...22 t/h that corresponds to capacity of existing tubular pyrolysis furnaces of mean capacity.

It is expediently to use gas-turbine engines of simple cycle applied at present in gas-turbine power stations and gas pumping stations of arterial gas pipelines. Full durability of such engines is usually 100,000 hours. Coefficient of efficiency of these engines is about 34...38 % and exhaust gas temperature is about 440...520 °C. High temperature of exhaust gas enables to use effectively its heat for preparation and preheating of feedstock-steam mixture and superheating of a steam for use in process needs. As fuel a natural gas or methane-hydrogen fraction separated from product stream in gas-fractionating installation can be used. Consumption of fuel gas per 1 ton of processed feedstock will not be greater than in tubular pyrolysis furnaces. Concentration of NO<sub>x</sub> in exhaust gases of stationary gas-turbine engines at present is of about 35...50 ppm that approximately 10 times less than concentrations NO<sub>x</sub> in smoke gases of tubular furnaces. The stationary gas-turbine engine with NO<sub>x</sub> emission of 6 ppm is already developed. So application of installations on base of rotary blade reactor enables essential improvement of ecological compatibility of ethylene plants.

It can be expected that more advantageous process conditions realized in rotary blade reactor in comparison with tubular furnace provide reduction in hydrocarbon feedstock consumption in low-molecular olefins production. Since pyrolysis installation on base of rotary blade reactor can be assembled on site of full readiness blocks delivered on place of construction by respective producers it should be expected that period and cost of construction will be in 2...3 times less in comparison with period and cost of construction for tubular furnace of similar capacity.

**Abstract**

(A process and apparatuses for producing low molecular olefins by pyrolysis of hydrocarbons comprising preheating and evaporating a starting feedstock, mixing the same with steam diluent, thermal cracking a resulting mixture in a blading rotary reactor, quenching cracked gas and subsequent separation of it. The heating reacting mixture to pyrolysis temperature is performed by mixing with hot pyrolyzed gas being circulated in a working cavity of the blading rotary reactor. The process enables to increase the low molecular olefins yield.)

**Process for producing low-molecular olefins by pyrolysis of hydrocarbons comprising mixing of feedstock with steam-diluent, preheating the resulting mixture, rapid heating the said mixture up to pyrolysis temperature and maintaining this temperature inside reactor during residence time, quenching product stream and subsequent fractionation of products. The reactor has an annular work cavity where stationary blades and rotatable work blades are located. A ring vortex flow is created and maintained in the work cavity when the work blades are rotated. A heat needed for pyrolysis is generated due to hydrodynamic drag of rotated work blades. Heating the mixture up to pyrolysis temperature is performed by mixing with hot process stream recirculated in the work cavity for a negligible time in comparison with the residence time. The process enables increase of the low-molecular olefins yield.**